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(12) Patent:

(11) CA 724612

(54) METHOD FOR PREPARING BANDAGES

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ABSTRACT

CLAIMS [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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(73) Owners: (Country)	NOBUHISA KAWAGUCHI (Not Available)
(71) Applicants: (Country)	
(74) Agent:	
(45) Issued:	1965-12-28
(22) Filed:	
(41) Open to Public Inspection:	1965-12-28
(52) Canadian Class (CPC):	117/187 28/0.53
(51) International Class (IPC):	N/A
Patent Cooperation Treaty (PCT):	No
(30) Application priority data:	None
Availability of licence:	N/A
Language of filing:	Unknown

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The present invention relates to the preparation of therapeutical, non-adhesive and ventilating materials.

The clinical treatment for cuts, scrapes, surgical incisions and other skin wounds generally employs dressings and other bandages which have three separate goals, namely: (1) ventilation of the wounded area, (2) absorption of blood, pus and other body fluids exuding from the wounded area and (3) protection of the wounded area from further physical damage. Optimum treating conditions require that these three goals be met.

Presently employed wound dressings include metal foils often used in skin grafting techniques. Such foils are quite non-adhesive hence do not produce additional physical damage such as by reopening the wound, but the foils are neither absorbent nor porous to the passage of air. The metal foils may actually retard healing.

Vaseline and similar petroleum jelly products have been employed to cover wounds. The vaseline is a good water repellent and when used in thin layers the vaseline allows ventilation of the wounded area. However, vaseline is quite adhesive to the wounded area and makes the job of dressing the wound and further application of medicaments a difficult task. Further, thick layers of vaseline impede the passage of air.

The object of this invention is to introduce a new wound dressing which is non-adhesive, ventilates the wound, and absorbs the fluids formed and exuded from the wound during the healing process. In short, the object of this invention is a new dressing for wounds which satisfies all of the requirements for such dressings.

*

This invention consists essentially of a method for the manufacture of therapeutical, non-adhesive, absorptive and ventilating surgical dressing consisting of the formation of an adherent cured coating of organopoly-siloxane on the surface fibers of a porous therapeutical surgical dressing. The coating is on the individual fibers so that the passage of air through the dressing is not disturbed.

The gauze materials employed as the surgical dressings of this invention must be substantially non-poisonous and may be of any desired color but are preferably white. Staple fibers such as cotton or wool are generally avoided in surgical dressing because fibers may drop from such materials and remain in the wound. The preferred gauzes are synthetic materials such as polyamide fibers, polyester fibers, acrylic fibers, cellulose acetate, vinylon, vinylformal and viscose. Also useful as gauzes in the method of this invention are hand-made Japanese paper, nylon paper, glass fiber and the like and other porous, spongy materials. The gauze must be resistant to the chemical and physical changes required to apply and cure the siloxane coating.

The siloxane polymers employed herein are polymeric materials having the general unit formula R_nSiO_{4-n} where n has an average value from 1 to 3 inclusive, preferably about 2, and each R represents a hydrogen atom or a monovalent hydrocarbon radical, at least 50 per cent of the R's being monovalent hydrocarbon radicals. The monovalent hydrocarbon radicals represented by R can be alkyl radicals such as methyl, ethyl and

octadecyl; aryl radicals such as phenyl and anthracyl;
cycloalkyl radicals such as cyclopropyl and cyclohexyl;
alkenyl radicals such as vinyl and allyl; alkaryl
radicals such as tolyl and xylyl; and aralkyl radicals
such as benzyl and phenylethyl. The siloxanes operable
herein can be homopolymers wherein all units are sub-
stantially identical, e.g. $[(CH_3)_2SiO]_x$, and they include
copolymers, e.g. some units may be $(CH_3)_2SiO$ units and the
balance may be $(CH_3)HSiO$ units. In any siloxane unit,
the R substituents can be the same or they can be
different. The operable polymers vary from water-thin
fluids to gumlike high polymers soluble in organic solvents.

It is preferable to include curing catalysts
with the siloxane and such catalysts include heavy metal
salts of carboxylic acids such as zinc, tin, iron, cobalt,
manganese, titanium and zirconium naphthenates, octoates,
and so forth. Also operative as catalysts are oxyhalides
of zinc, tin, iron, cobalt, manganese, titanium,
zirconium and other heavy metals as well as organic
peroxides, organic amines, ammonia, alkalies, zirconium
and titanium esters, inorganic bases and other materials
heretofore known as catalysts for curing siloxane polymers
to the infusible insoluble state. One excellent method
for securing sterile dressings while curing the siloxane
coating is to expose the dressing treated with siloxane to
high energy ionizing radiation as from a Van de Graaff
particle accelerator or Co-60 source.

The preferred siloxane polymers are diorgano-
siloxanes of unit formula R_2SiO and organohydrogensilox-
anes of unit formula $RHSiO$ where R is as above defined.

Copolymers and mixtures of polymers of such units are excellent for this purpose. Such polymers are available at commercially attractive prices, in large quantities with an excellent degree of purity. The most preferred polymers are substituted with methyl, ethyl, vinyl and/or phenyl substituents with hydrogen substituents optional. These polymers are prepared by methods well known in the art and widely practiced by industry.

The siloxane with or without catalyst can be applied to the gauze by any desired method. Suggested methods include application from solution, emulsion or as undiluted liquid siloxane. Optionally, the lower siloxane polymers can be applied as vapors. Application by spraying, dipping, flowing, padding or any other method can be employed. The treated dressing is usually heated at 90° to 200°C. to cure the siloxane coating but if the coating will cure at room temperature this heating step can be avoided.

The siloxane can be used alone or in conjunction with organic resins such as ureaform resins, melamine resins, vinylic resins and surface active substances.

A useful technique for applying the siloxane comprises moistening with water the gauze or sponge to be treated. The wet material is then exposed to vapors of hydrolyzable organosilane of the formula R_nSiX_{4-n} where R and n are as above defined and X is a hydrolyzable atom or group such as halogen atoms and alkoxy groups. In situ hydrolysis of the silane produces the desired siloxane coating on the fibers.

The treated dressings, which may be sponge-like materials as well as the more familiar gauze-like materials, are absorbent and effectively retain blood, pus and other fluids in connection with body wounds. The treated dressings also permit the flow of air to the wound thus providing the desired ventilation and the dressings are readily removed from the wounded area permitting further treatment without causing damage to the wounded area. The reasons for the easy removal of the treated dressings are not fully understood because the healing mechanism is not sufficiently clarified. It is apparent the water repellency imparted to the dressings by this method is not the full answer because other materials such as waxes, fats and oils also impart water repellency to bandages but bandages so treated are not readily removed from the wounded area. It is believed the combination of water repellency, known release characteristics and the inertness toward body tissues and fluid exhibited by siloxane polymers contributes to the desired non-adhesion of the treated dressings to the wounded area.

The examples following are included herein to aid those skilled in the art in understanding and practicing this invention. All parts and percentages in the examples are based on weight and all viscosities were measured at room temperature unless otherwise indicated. The symbols Me, Et and Vi represent the methyl, ethyl and vinyl radicals.

Example 1

A trimethylsilyl endblocked methylhydrogen-siloxane was mixed with a trimethylsilyl endblocked dimethylsiloxane of 100 poise viscosity in a molar ratio

of 3.5 mols MeHSiO units per mol of Me₂SiO units. 10 parts of the mixture and 0.2 parts tin octoate were dissolved in 90 parts chloroform. A handwoven glass fabric of .7 mil thickness was dipped into the solution with a pickup of about 1 per cent siloxane. The cloth was air dried and heated at 145°C. for 10 minutes to cure the siloxane. A sterile dressing made from this treated cloth was applied to a wounded skin surface after skin-grafting. The dressing was removed after one week. The dressing was easily removed from the wounded surface without pain to the patient and without any damage whatsoever to the wounded area. The secretion of fluids from the wounded area was readily absorbed with cotton gauze placed on the reverse side of the dressing. The healing effect was extremely good.

Dressings made entirely from the treated glass cloth were also prepared and used with excellent results.

Example 2

A polyurethane sponge of 10 mm. thickness and having an apparent specific gravity of 0.04 and perforated with holes was sprayed on both sides with a 10 per cent benzol solution of methylhydrogensiloxane having a viscosity of .5 poises. The solution sprayed on the sponge did not penetrate to the inner portion of the sponge and the treatment was restricted to the surface layers of the sponge. The treated sponge was air dried for two hours to remove the solvent and the siloxane was cured by heating at 150°C. for 10 minutes. The resulting sponge was pressed on an abraded skin area during a hair-implantation. The sponge absorbed the body fluids from the wound, permitted

ventilation of the skin surface and was easily removed from the wounded area after one week. The removal of the sponge caused no pain and resulted in no damage to the wounded area.

5 Example 3

 A mixture of 40 parts methylhydrogensiloxane of .5 poise viscosity and 60 parts dimethylsiloxane gum having a Williams plasticity of .050 was dissolved in 400 parts naphtha. This mixture was specified as Liquid A.
10 A mixture of 100 parts liquid A and 0.5 parts benzoyl peroxide was dissolved in about 500 parts perchlorethylene and applied to a handwoven Japanese paper. The treated paper was air dried for 30 minutes and heated to 120°C. for 4 minutes. The Japanese paper so coated was employed
15 as a dressing on skin being treated by sand paper plastic surgery methods. The coated paper was easily removed from the abraded skin for further treatment.

Example 4

 A mixture of 100 parts liquid A, 10 parts zinc octoate, 100 parts trichlorethylene, 5 parts emulsifying agent and 210 parts water was emulsified employing a high speed mixer. A nylon Taffeta was dipped in the emulsion and heated at 150°C. for 15 minutes. Dressings made from the treated cloth were employed to cover burned skin areas.
20 The dressings exhibited excellent release from the wounded areas covered and were readily penetrated by liquids secreting from the wound.
25

Example 5

 A trimethylsilyl endblocked methylhydrogen-
30 siloxane having 7 mol per cent trimethylsilyl units and

93 mol per cent methylhydrogensiloxane units was emulsified with 10 parts methylphenylsiloxane having a viscosity of 150 poises, 10 parts benzol and 10 parts of a sulfonate of lauryl alcohol in 192 parts water. A mixture was prepared from 30 parts of the emulsion, 100 parts denaturized methylolmelamine resin and 300 parts water. A catalytic amount of zinc as zinc octoate was added to the mixture and a polyester cellulose fabric of 3 mil thickness was dipped in the liquid. The treated fabric was air dried and the siloxane cured by heating at 160°C. for 3 minutes. The cloth was applied to an area of burned skin and exhibited excellent release from the burned area. The cloth was washed with warm water and soap, rinsed, dried, sterilized at 120°C. with steam under pressure and reused with excellent results.

Example 6

A tricot knit acetate fabric was treated in accordance with Example 5 employing a solution of 7 parts diethylsiloxane of 5 poise viscosity, .3 parts methylvinylsiloxane gum, 0.1 part tetrabutyltitanate and 150 parts methylenechloride. The cloth picked up 3.75 per cent of its weight of non-volatile solids. The wet cloth was air dried for 72 hours. The treated cloth was used as a dressing on a surgical incision and exhibited excellent release from a wound.

Example 7

A polyurethane sponge as in Example 2 was moistened with water and thereafter was exposed to vapors of methylhydrogendieethoxysilane for 25 hours. The sponge was heated at 120°C. for 20 minutes. The sponge was

employed for oppressing in dermatological surgery and showed excellent release from the skin area.

Example 8

A handwoven glass fabric of 7 mil thickness was heat cleaned, then dipped in water and as so moistened was exposed for 1 hour to vapors of a mixture of 2 mols Me_2SiCl_2 and 3 mols MeSiCl_3 . The fabric was then heated at 220°C . for 4 hours. The fabric was used to dress a surgical incision and was easily removed from the wounded skin even after several days of healing.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A bandage or wound dressing which is air-pervious, absorbent and non-adhesive to wounds and surgical incisions comprising a surgical dressing coated with a cured film of organosiloxane polymer.

2. The wound dressing of claim 1 further characterized in that the organosiloxane polymer has the unit formula $R_nSiO_{\frac{4-n}{2}}$ where each R is a hydrogen atom or monovalent hydrocarbon radical and n has an average value of from 1 to 3 inclusive.

3. The wound dressing of claim 1 further characterized in that a mixture of organosiloxane polymer and amide type condensed resin or resinous vinyllic polymer is employed as a coating.

4. The wound dressing of claim 2 further characterized in that the wound dressing is made of polyamide fiber, polyester fiber, acrylic fiber, viscose, cellulose acetate, glass fiber, polyurethane foam or Japanese paper.

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Language of filing:	Unknown

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The clinical treatment for cuts, scrapes, surgical incisions and other skin wounds generally employs dressings and other bandages which have three separate goals, namely: (1) ventilation of the wounded area, (2) absorption of blood, pus and other body fluids exuding from the wounded area and (3) protection of the wounded area from further physical damage. Optimum treating conditions require that these three goals be met.

Presently employed wound dressings include metal foils often used in skin grafting techniques. Such foils are quite non-adhesive hence do not produce additional physical damage such as by reopening the wound, but the foils are neither absorbent nor porous to the passage of air. The metal foils may actually retard healing.

Vaseline and similar petroleum jelly products have been employed to cover wounds. The vaseline is a good water repellent and when used in thin layers the vaseline allows ventilation of the wounded area. However, vaseline is quite adhesive to the wounded area and makes the job of dressing the wound and further application of medicaments a difficult task. Further, thick layers of vaseline impede the passage of air.

The object of this invention is to introduce a new wound dressing which is non-adhesive, ventilates the wound, and absorbs the fluids formed and exuded from the wound during the healing process. In short, the object of this invention is a new dressing for wounds which satisfies all of the requirements for such dressings.

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This invention consists essentially of a method for the manufacture of therapeutical, non-adhesive, absorptive and ventilating surgical dressing consisting of the formation of an adherent cured coating of organopoly-siloxane on the surface fibers of a porous therapeutical surgical dressing. The coating is on the individual fibers so that the passage of air through the dressing is not disturbed.

The gauze materials employed as the surgical dressings of this invention must be substantially non-poisonous and may be of any desired color but are preferably white. Staple fibers such as cotton or wool are generally avoided in surgical dressing because fibers may drop from such materials and remain in the wound. The preferred guazes are synthetic materials such as polyamide fibers, polyester fibers, acrylic fibers, cellulose acetate, vinylon, vinylformal and viscose. Also useful as gauzes in the method of this invention are hand-made Japanese paper, nylon paper, glass fiber and the like and other porous, spongy materials. The gauze must be resistant to the chemical and physical changes required to apply and cure the siloxane coating.

The siloxane polymers employed herein are polymeric materials having the general unit formula $R_nSiO_{4-\frac{n}{2}}$ where n has an average value from 1 to 3 inclusive, preferably about 2, and each R represents a hydrogen atom or a monovalent hydrocarbon radical, at least 50 per cent of the R 's being monovalent hydrocarbon radicals. The monovalent hydrocarbon radicals represented by R can be alkyl radicals such as methyl, ethyl and

octadecyl; aryl radicals such as phenyl and anthracyl;
cycloalkyl radicals such as cyclopropyl and cyclohexyl;
alkenyl radicals such as vinyl and allyl; alkaryl
radicals such as tolyl and xylyl; and aralkyl radicals
such as benzyl and phenylethyl. The siloxanes operable
herein can be homopolymers wherein all units are sub-
stantially identical, e.g. $[(CH_3)_2SiO]_x$, and they include
copolymers, e.g. some units may be $(CH_3)_2SiO$ units and the
balance may be $(CH_3)HSiO$ units. In any siloxane unit,
the R substituents can be the same or they can be
different. The operable polymers vary from water-thin
fluids to gumlike high polymers soluble in organic solvents.

It is preferable to include curing catalysts
with the siloxane and such catalysts include heavy metal
salts of carboxylic acids such as zinc, tin, iron, cobalt,
manganese, titanium and zirconium naphthenates, octoates,
and so forth. Also operative as catalysts are oxyhalides
of zinc, tin, iron, cobalt, manganese, titanium,
zirconium and other heavy metals as well as organic
peroxides, organic amines, ammonia, alkalies, zirconium
and titanium esters, inorganic bases and other materials
heretofore known as catalysts for curing siloxane polymers
to the infusible insoluble state. One excellent method
for securing sterile dressings while curing the siloxane
coating is to expose the dressing treated with siloxane to
high energy ionizing radiation as from a Van de Graaff
particle accelerator or Co-60 source.

The preferred siloxane polymers are diorgano-
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anes of unit formula $RHSiO$ where R is as above defined.

Copolymers and mixtures of polymers of such units are excellent for this purpose. Such polymers are available at commercially attractive prices, in large quantities with an excellent degree of purity. The most preferred polymers are substituted with methyl, ethyl, vinyl and/or phenyl substituents with hydrogen substituents optional. These polymers are prepared by methods well known in the art and widely practiced by industry.

The siloxane with or without catalyst can be applied to the gauze by any desired method. Suggested methods include application from solution, emulsion or as undiluted liquid siloxane. Optionally, the lower siloxane polymers can be applied as vapors. Application by spraying, dipping, flowing, padding or any other method can be employed. The treated dressing is usually heated at 90° to 200°C. to cure the siloxane coating but if the coating will cure at room temperature this heating step can be avoided.

The siloxane can be used alone or in conjunction with organic resins such as ureaform resins, melamine resins, vinylic resins and surface active substances.

A useful technique for applying the siloxane comprises moistening with water the gauze or sponge to be treated. The wet material is then exposed to vapors of hydrolyzable organosilane of the formula R_nSiX_{4-n} where R and n are as above defined and X is a hydrolyzable atom or group such as halogen atoms and alkoxy groups. In situ hydrolysis of the silane produces the desired siloxane coating on the fibers.

The treated dressings, which may be sponge-like materials as well as the more familiar gauze-like materials, are absorbent and effectively retain blood, pus and other fluids in connection with body wounds. The treated dressings also permit the flow of air to the wound thus providing the desired ventilation and the dressings are readily removed from the wounded area permitting further treatment without causing damage to the wounded area. The reasons for the easy removal of the treated dressings are not fully understood because the healing mechanism is not sufficiently clarified. It is apparent the water repellency imparted to the dressings by this method is not the full answer because other materials such as waxes, fats and oils also impart water repellency to bandages but bandages so treated are not readily removed from the wounded area. It is believed the combination of water repellency, known release characteristics and the inertness toward body tissues and fluid exhibited by siloxane polymers contributes to the desired non-adhesion of the treated dressings to the wounded area.

The examples following are included herein to aid those skilled in the art in understanding and practicing this invention. All parts and percentages in the examples are based on weight and all viscosities were measured at room temperature unless otherwise indicated. The symbols Me, Et and Vi represent the methyl, ethyl and vinyl radicals.

Example 1

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of 3.5 mols MeHSiO units per mol of Me₂SiO units. 10 parts of the mixture and 0.2 parts tin octoate were dissolved in 90 parts chloroform. A handwoven glass fabric of .7 mil thickness was dipped into the solution with a pickup of about 1 per cent siloxane. The cloth was air dried and heated at 145°C. for 10 minutes to cure the siloxane. A sterile dressing made from this treated cloth was applied to a wounded skin surface after skin-grafting. The dressing was removed after one week. The dressing was easily removed from the wounded surface without pain to the patient and without any damage whatsoever to the wounded area. The secretion of fluids from the wounded area was readily absorbed with cotton gauze placed on the reverse side of the dressing. The healing effect was extremely good.

Dressings made entirely from the treated glass cloth were also prepared and used with excellent results.

Example 2

A polyurethane sponge of 10 mm. thickness and having an apparent specific gravity of 0.04 and perforated with holes was sprayed on both sides with a 10 per cent benzol solution of methylhydrogensiloxane having a viscosity of .5 poises. The solution sprayed on the sponge did not penetrate to the inner portion of the sponge and the treatment was restricted to the surface layers of the sponge. The treated sponge was air dried for two hours to remove the solvent and the siloxane was cured by heating at 150°C. for 10 minutes. The resulting sponge was pressed on an abraded skin area during a hair-implantation. The sponge absorbed the body fluids from the wound, permitted

ventilation of the skin surface and was easily removed from the wounded area after one week. The removal of the sponge caused no pain and resulted in no damage to the wounded area.

5 Example 3

 A mixture of 40 parts methylhydrogensiloxane of .5 poise viscosity and 60 parts dimethylsiloxane gum having a Williams plasticity of .050 was dissolved in 400 parts naphtha. This mixture was specified as Liquid A.
10 A mixture of 100 parts liquid A and 0.5 parts benzoyl peroxide was dissolved in about 500 parts perchlorethylene and applied to a handwoven Japanese paper. The treated paper was air dried for 30 minutes and heated to 120°C. for 4 minutes. The Japanese paper so coated was employed
15 as a dressing on skin being treated by sand paper plastic surgery methods. The coated paper was easily removed from the abraded skin for further treatment.

Example 4

 A mixture of 100 parts liquid A, 10 parts zinc octoate, 100 parts trichlorethylene, 5 parts emulsifying
20 agent and 210 parts water was emulsified employing a high speed mixer. A nylon Taffeta was dipped in the emulsion and heated at 150°C. for 15 minutes. Dressings made from the treated cloth were employed to cover burned skin areas.
25 The dressings exhibited excellent release from the wounded areas covered and were readily penetrated by liquids secreting from the wound.

Example 5

 A trimethylsilyl endblocked methylhydrogen-
30 siloxane having 7 mol per cent trimethylsilyl units and

93 mol per cent methylhydrogensiloxane units was emulsified with 10 parts methylphenylsiloxane having a viscosity of 150 poises, 10 parts benzol and 10 parts of a sulfonate of lauryl alcohol in 192 parts water. A mixture was prepared from 30 parts of the emulsion, 100 parts denaturized methylolmelamine resin and 300 parts water. A catalytic amount of zinc as zinc octoate was added to the mixture and a polyester cellulose fabric of 3 mil thickness was dipped in the liquid. The treated fabric was air dried and the siloxane cured by heating at 160°C. for 3 minutes. The cloth was applied to an area of burned skin and exhibited excellent release from the burned area. The cloth was washed with warm water and soap, rinsed, dried, sterilized at 120°C. with steam under pressure and reused with excellent results.

Example 6

A tricot knit acetate fabric was treated in accordance with Example 5 employing a solution of 7 parts diethylsiloxane of 5 poise viscosity, .3 parts methylvinylsiloxane gum, 0.1 part tetrabutyl titanate and 150 parts methylenechloride. The cloth picked up 3.75 per cent of its weight of non-volatile solids. The wet cloth was air dried for 72 hours. The treated cloth was used as a dressing on a surgical incision and exhibited excellent release from a wound.

Example 7

A polyurethane sponge as in Example 2 was moistened with water and thereafter was exposed to vapors of methylhydrogendieethoxysilane for 25 hours. The sponge was heated at 120°C. for 20 minutes. The sponge was

employed for oppressing in dermatological surgery and showed excellent release from the skin area.

Example 8

5 A handwoven glass fabric of 7 mil thickness was
heat cleaned, then dipped in water and as so moistened
was exposed for 1 hour to vapors of a mixture of 2 mols
10 Me_2SiCl_2 and 3 mols MeSiCl_3 . The fabric was then heated
at 220°C . for 4 hours. The fabric was used to dress a
surgical incision and was easily removed from the wounded
skin even after several days of healing.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A bandage or wound dressing which is air-pervious, absorbent and non-adhesive to wounds and surgical incisions comprising a surgical dressing coated with a cured film of organosiloxane polymer.

2. The wound dressing of claim 1 further characterized in that the organosiloxane polymer has the unit formula $R_nSiO_{4-\frac{n}{2}}$ where each R is a hydrogen atom or monovalent hydrocarbon radical and n has an average value of from 1 to 3 inclusive.

3. The wound dressing of claim 1 further characterized in that a mixture of organosiloxane polymer and amide type condensed resin or resinous vinylic polymer is employed as a coating.

4. The wound dressing of claim 2 further characterized in that the wound dressing is made of polyamide fiber, polyester fiber, acrylic fiber, viscose, cellulose acetate, glass fiber, polyurethane foam or Japanese paper.

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